Vibronic Interaction and Vibrational Assignment for NO_3 in the Ground Electronic State

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VA-1. Stanton's ν_3 spurious ! (near 1000 cm^{-1} *vs* 1492 cm^{-1})

(1) IR absorption (Kawaguchi, Ishiwata, Hirota)

700~1500 cm^{-1} no ν_3 band

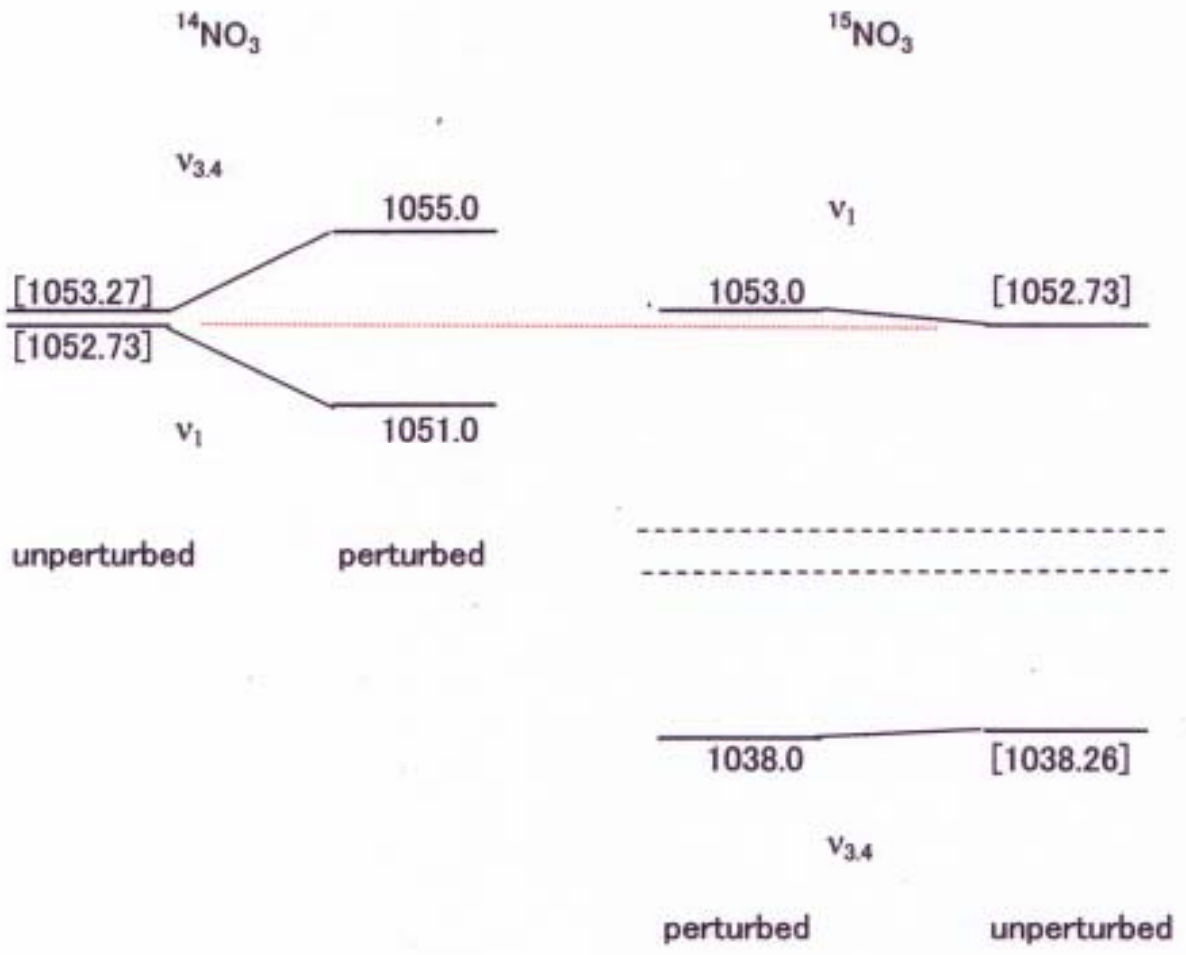
(2) LIF (Fukushima, Ishiwata)

	ν_1	"new"(cm^{-1})
$^{14}NO_3$	1051	1055
$^{15}NO_3$	1053	1038

"new" $\neq \nu_3$ no ν_3 band

$= 3\nu_4(a')$

$k_{1444} = 1.618$, $\nu_1^\circ = 1052.773$


$^{14}NO_3$
$^{15}NO_3$
$\nu_{3,4}$
1055.0
ν_1
[1053.27]
1053.0
[1052.73]
[1052.73]
ν_1
1051.0
unperturbed
perturbed
1038.0
[1038.26]
$\nu_{3,4}$
perturbed
unperturbed

VA-2. only one $A-E$ type $Z-\nu_4$ hot band (Z: the upper state of the 1492 cm^{-1} band)

Assignment II Stanton-Jacox

$Z = \nu_3 + \nu_4$ A_1, A_2, E

one $E-E$ and two $A-E$ are expected, but no explanation has been given !

Assignment I traditional

$Z = \nu_3, (2\nu_2)$

one $E-E$: $\nu_3 - \nu_4$ and one $A-E$: $2\nu_2 - \nu_4$

Cf. ν_2 = 762.34045 (742.71195) ($^{15}NO_3$)

x 2 = 1524.6809 (1485.4239)

Obs. $A-E$ 1499.7493 (1475.1072)

(4/3) x $[3\nu_4(a')]_{av}$ 1512.(1488)

VA-3. Molecular parameters in *Z*, the upper state of the1492 cm^{-1} band

Assignment II ($\nu_3 + \nu_4$)

ν_4 ℓ-type doubling const. q_4

obs. 0.001094 [cf. 0.0133024 in ν_4]

First-order Coriolis coupling constant ζ

obs. (*E* state) −0.19006 [$\zeta_3 + \zeta_4 = 0.0$]

No reasonable explanations have been provided, indicating that

Assignment II is not acceptable !

VA-4. ν_4 progression in the photoelectron spectrum of NO_3^-

Neumark *et al.* (1991)

Herzberg-Teller effect via ν_4

Stanton (2007, 2009) ab initio

too large H-T parameters

distortion in PES of ν_4 in the GS

Stanton's anharmonicity constants excessive

No anomalies found in the ν_4 rot. structure

How can we explain the ν_4 progression by Assignment I ?

Our previous study on NO_3:

E. Hirota et al., *J. Chem. Phys.* **95**, 771 (1991)

Vibronic interaction between X^2A_2' and B^2E'

$$\mathbf{H_{ve}} = V_1 q\{\exp[i(\theta - \alpha)] + \exp[-i(\theta - \alpha)]\}$$
$$+ V_2 q^2\{\exp[i(\theta + 2\alpha)] + \exp[-i(\theta + 2\alpha)]\} + \ldots$$

θ : unpaired electron, α : deg.normal mode(ν_3, ν_4)

2nd-order perturb. $h_1, h_2 << E(B - X) = 15000\ \mathrm{cm}^{-1}$

$h_1 = \langle B|V_1|X\rangle$, $h_2 = \langle B|V_2|X\rangle$,

$$V_{\mathrm{eff}} = (\omega/2)q^2 - (|h_1|^2/E)q^2$$
$$- (|h_1 h_2|/E)(q_+^3 + q_-^3) + \ldots$$

$$q_\pm = q\exp(\pm i\theta)$$

VR-1. Correlation between the first-order Coriolis coupling const. and the effective spin-orbit interaction constant

NOTE

These observations apply only to

Assignment I, but not to Assignment II !

Suggesting a new type of vibronic interaction

First-order Coriolis coupling constant and spin-orbit interaction constant $^{14}NO_3$

Band	ν_0 [d]	ζ	a_{eff} [e]
ν_4 [a]	365.4840	–0.18743	–0.16888
$3\nu_4(E)$ [b]	1173.6141	–0.24887	–0.0991
$\nu_1+\nu_4$ [b]	1413.5686	–0.11574	–0.13665
ν_3 [a]	1492.39356	+0.19125	+0.17066
$\nu_1+\nu_3$ [c]	2518.7130	+0.10190	+0.13290

[a] Present study.

[b] T. Ishiwata, unpublished.

[c] T. Ishiwata, I. Tanaka, K. Kawaguchi, and E. Hirota, *J. Mol. Spectrosc.* **153**, 167 (1992).

[d] Band origin, in cm^{-1}.

[e] Effective spin-orbit coupling constant [$a_{eff}L_cS_c$], in cm^{-1}.

First-order Coriolis coupling constant and spin-orbit interaction constant $^{15}NO_3$

Band	ν_0 [d]	ζ	a_{eff} [e]
ν_4 [a]	360.1996	–0.1557	–0.1657
$3\nu_4(E)$ [b]	1159.2456	–0.21122	–0.1065
$\nu_1+\nu_4$ [b]	1407.0273	–0.06977	–0.12737
ν_3 [a]	1472.8242	+0.1509	+0.1585
$\nu_1+\nu_3$ [c]	2492.9587	+0.10306	+0.07876

[a] Present study.

[b] T. Ishiwata, unpublished.

[c] T. Ishiwata, Y. Nakano, K. Kawaguchi, E. Hirota, and I. Tanaka, *J. Phys. Chem.* A**114**, 980 (2010).

[d] Band origin, in cm^{-1}.

[e] Effective spin-orbit coupling constant [$a_{eff}L_cS_c$], in cm^{-1}.

VR-2. Harmonic force field must include the contributions of the unpaired electron

Care should be taken of this fact in calculating isotopic shifts

Inertial defect and centrifugal distortion constant of NO_3 in the ground vibronic state

	Calc		obs
ζ_3	= 0.193	= 0.7	
Inertial defect(uÅ^2)	0.2221	0.2585	0.2193(64)
D_N (10^{-5} cm^{-1})	0.1069	0.1421	0.1058(49)
D_{NK} (10^{-5} cm^{-1})	–0.1965	–0.2667	–0.162(11)

VR-3. New-type of vibronic interaction

linear polyatomic free radical in $^2\Sigma$

in excited state of bending $\rightarrow$ $^2\Pi$

symmetric-top free radical in ^2A

in excited state of degenerate mode

$\rightarrow$ ^2E

bearing the character of a ^2E excited electronic state

So far almost no examples have been known !

VR.-4. A new vibronic interaction model (1)

Unpaired electron orbital in the ground electronic state

The a_2' orbital consists of

a radial part $R(r)$ and an azimuthal part $\Theta(\theta)$

in the *A*-type vibrational states

Θ has no θ dependence; cylindrical sym.

but, when a degenerate mode of *E* symmetry is excited,

Θ includes a finite angular momentum (electronic and vibrational), as defined by

$\overline{\Lambda} = \Lambda + \ell = \pm 1$

A new vibronic interaction model (2)

Total wavefuntion: $|e\rangle|v\rangle|\bar{\Lambda}\rangle$,

rather than conventional $|e, \Lambda\rangle|v, \ell\rangle$

$|e\rangle|v\rangle$: only radial part

The effective spin-orbit term

mainly from the “diagonal” matrix elements

Degenerate vibrational states in the ground electronic state behave as degenerate electronic states,

contribute to the photoelectron spectra of NO_3^-.

$3\nu_4$ states around 1050 cm^{-1}

isotopic species		$^{14}NO_3$	$^{15}NO_3$
$3\nu_4(a')$	$\lvert\ell_4\rvert=3$	1055	1038
Diff.		122	122
$3\nu_4(e')$	$\lvert\ell_4\rvert=1$	1177	1160
Diff.		37	34
$3\nu_4(a')$	$\lvert\ell_4\rvert=3$	1214	1194

large splitting for $|\ell_4|=3$

$(2/3)[3\nu_4(a')]_{av}$	756	744
$2\nu_4(a')$	754	744

Future

1. $\nu_2/2\nu_4$ Coriolis interactions

   No transitions have been assigned for $2\nu_4$

2. Obs. and analysis of $3\nu_4(a') - \nu_4$

   and $\nu_1 - \nu_4$

3. New vibronic interaction

   theoretical formulation required

   on electron–nuclear interactions